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## Characterization and 3D printability of poly (lactic acid)/acetylated tannin composites

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**Abstract:** In this study, a three-dimensional (3D) printing filament prepared from 11 12 poly (lactic acid) (PLA) and acetylated tannin via a twin-screw extruder was reported. The impact of acetylated tannin loading content on the final properties of the 13 resulting composite materials and their 3D printability were investigated. The 14 experimental results indicate that PLA can be compounded with up to 20 wt% 15 acetylated tannin without any obvious deterioration in the tensile property. The 16 resulting composites acquired better degradation rate in aquatic system compared 17 with neat PLA, especially in alkaline medium. Moreover, all composites are printable 18 19 and showed generally good printing quality with brown color, however, this is 20 limited to temperatures reasonably below 220°C to avoid printing defects, especially at high loadings of acetylated tannin. 21

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Keywords: poly (lactic acid), acetylated tannin, composite, degradation, 3D
 printability

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#### 26 1. Introduction

Additive manufacturing, commonly known as three-dimensional (3D) printing, is a promising manufacturing technology whose related numerous applications have been explored in the fields like construction, manufacturing, healthcare and medicine, art and fashion, food industry (Lee et al., 2017; Liu et al., 2019). With this technique, customized complex and high-resolution three-dimensional parts can be rapidly built through

successive layer-by-layer deposition of materials like plastic, metal, ceramics, or living
 cells (Tappa and Jammalamadaka, 2018). For producing thermoplastics prototype parts,
 fused deposition modeling (FDM) or melt-extrusion 3D printing is the most widely used
 additive manufacturing technique.

Polylactic acid (PLA) is one of the most popular 3D printing thermoplastic materials 36 due to its printability, favorable mechanical properties, and biocompatibility. It is an 37 renewable and biodegradable polyester that can be synthesized directly through 38 39 polycondensation of lactic acids or ring-opening polymerization of lactides (Ren, 2011). 40 PLA can be also incorporated with sustainable materials or biopolymers (e.g. wood powder, plant fiber, cellulose, lignin, hemicellulose) for the purpose of reinforcing 41 and/or specific functions, and/or reducing cost. However, studies of these PLA-based 42 bio-composites as 3D printing materials are still limited (Bajpai et al., 2014; Basu et al., 43 2017; Murariu and Dubois, 2016). Sustainable materials or biopolymers applied as 3D 44 printing feedstock are promising substitutes for fossil-based fillers due to their 45 sustainability, biodegradability, and cost-efficient characteristics. For instance, the 46 47 presence of wood powder in 3D printing, PLA filaments displays higher stiffness and less abrasive properties compared to other composite filaments, such as carbon-fiber filled 48 PLA filaments and metal-filled PLA filaments (Guo et al., 2018). Fibers derived from 49 50 wood, bamboo, and cellulose were also investigated as feedstock for PLA-based filaments because of their positive effects on the mechanical properties and heat 51 resistance of PLA matrix (LI et al., 2016; Long et al., 2019). Hemicellulose has been 52 53 investigated to partially replace PLA as feedstock material in 3D printing (Xu et al., 54 2018). This combination makes use of the characteristics of hemicelluloses such as biocompatibility, biodegradability, and presence of versatile active sites for biomedical 55 56 applications. PLA combined with lignin has attracting characteristics such as antioxidant, antifungal and antimicrobial capacities, resistance to UV-radiation, and fire-retardant 57 properties (Kai et al., 2016). One example was reported to study PLA/lignin composites 58 59 for 3D printing (Gkartzou et al., 2017). However, the lignin aggregation and its low 60 compatibility with PLA matrix caused imperfect printed objects and surface roughness,

even at low loading content (5 wt%.). According to the published literature as yet, it
appears that the dispersion and distribution of fillers are key factors for processing 3D
printing materials (Nguyen et al., 2018).

64 Condensed tannins are interesting abundant and sustainable biopolymers for 3D printing, however, there is no related research work about their applications in the field 65 of 3D printing to date. Condensed tannins are mainly composed of flavonoid units in 66 varying degrees of condensation (Erreur ! Source du renvoi introuvable.) and they can 67 be easily extracted from soft tissues of woody plants like leaves, needles, and bark using 68 69 water or organic solvent (Pizzi, 1980). They display great potential as component of PLA bio-composites due to some interesting characteristics like antioxidant (Koleckar et al., 70 2008), antimicrobial (Ge et al., 2003) and stabilizing properties (Liao et al., 2019; Olejar 71 72 et al., 2016; Tomak et al., 2018). Over the past few years, tannins have been 73 investigated as functional additives or at least a component of polymeric composites. 74 For instance, tannins have been reported as stabilizing additive with antioxidant and UV-75 protective properties on polypropylene (Ambrogi et al., 2011; Samper et al., 2013), 76 polyethylene (Bridson et al., 2015), poly(vinylchloride) (PVC) (Shnawa et al., 2015), and polyvinyl alcohol (Zhai et al., 2018). Anwer reported a native tannin as a filling 77 component of PLA composite material (Anwer et al., 2015), where poor adhesion 78 79 between tannin and PLA matrix as well as dispersion of tannin in PLA were found, thereby, poor tensile strength was noticed even at higher filler content (15%). 80 Modifications of tannins, like esterification and hydroxypropylation, have been proved 81 82 to enhance the compatibility and dispersion capacity to various plastics (D. E. García et 83 al., 2015; Gaugler et al., 2007; Grigsby et al., 2014, 2015, 2013; Grigsby and Kadla, 2014). Grigsby and co-workers (Grigsby et al., 2015) modified tannin with ester-bearing long 84 85 chain, which lowered the melting temperature and claimed this could significantly reduce the incompatibility with PLA matrix, leading meanwhile to easier processability. 86 However, the substitution of higher chain length on tannin flavonoid units becomes 87 progressively more difficult due to the elevated steric hindrance. In another extended 88 89 study, Grigsby carried out a high loading content of esterified tannin (50%) as

90 reinforcing material for PLA fine fiber processed via melt spinning in the presence of 91 transesterification catalyst (Grigsby and Kadla, 2014). This successful incorporation of 92 esterified tannin onto PLA indicated the possibility to process esterified tannin filled PLA 93 filaments for 3D printing. Esterification can reduce the hydrophilicity of tannin, reducing 94 the clogging at the printing nozzle and discontinuous layer deposition during printing 95 process due to good dispersion and distribution of tannin onto the polymer matrix.



96 97

Figure 1. Structure of four main flavonoid units of condensed tannins

The present study will focus on developing a new approach to utilize condensed 98 99 tannin obtained from mimosa wood barks for partial replacement of PLA in 3D printing parts and investigate the feasibility of melt-extrusion 3D printing. For this purpose, 100 101 mimosa tannin was acetylated to decrease its initial hydrophilicity. Such treatment has been proven to enhance the compatibility of tannin and thermoplastic polymeric 102 103 matrixes without severe agglomeration (Gaugler et al., 2007; Grigsby et al., 2013). The 104 composite was processed in a twin-screw extruder and the impact of the loading level of acetylated tannin (AT) on the final properties of the resulting composite materials was 105 106 evaluated in terms of the tensile property, the changes in crystallization, thermal 107 degradation, changes in color, and degradation rate in aquatic system. Besides, the feasibility of melt-extrusion 3D printing of PLA/AT composite was also investigated. 108

109 **2.** Materials and Methods

#### 110 2.1. Materials

111 PLA trademarked under the name IngeoTM Biopolymer (Grade 3D850) with a melt 112 flow index of 7-9 g/10min was obtained from Nature works LLC (Minnesota, USA). 113 Mimosa tannins were purchased from Silva Chimica, Mondovi, Italy. Acetic anhydride

used to acetylate tannin and pyridine, a catalyst for tannin acetylation, were supplied
from Sigma-Aldrich and Acros-Organics, respectively. Three buffers purchased from
Sigma-Aldrich were used for degradation tests, including phosphate buffer (pH=4.0),
sodium carbonate buffer (pH=10.0), and phosphate Buffered Saline (PBS, pH=7.4).

118 2.2. Preparation of PLA/AT Composites

#### 119 2.2.1. Tannin acetylation

Acetylation of mimosa tannin was described elsewhere by using acetic anhydride and pyridine as catalyst (Nicollin et al., 2013). Mimosa tannin was mixed with acetic anhydride in a weight ratio of 1:5 with 1 wt% pyridine (based on tannin) as catalyst in a round bottom flask fitted with a condenser. The mixture was heated to 60°C under stirring for 6 h. After the acetylation is achieved, the suspension was precipitated in iced water and centrifuged to recover the acetylated tannin powder, which was washed 5 times with distilled water and finally air-dried at room temperature for several days.

#### 127 2.2.2. Composite filament preparation

128 PLA was ground into powder by a grinder to ensure simplistic mixing with tannin. Then, PLA and acetylated tannin (AT) powder were dried in an oven at 80°C for more 129 than 12 h to remove any absorbed water on the surface. A twin-screw extruder (Thermo 130 Scientific<sup>™</sup> Process 11, Villebon-Sur-Yvette, France) was used to blend PLA powder and 131 AT. Two mixing zones of screw profile can guarantee high level of homogeneous 132 dispersion of AT in PLA. The temperature of the heating zones and the die along the 133 134 extruder barrel ranged are shown in Figure 2. The filaments were extruded through melt blending extrusion with a rotation rate of 80 rpm via a nozzle diameter of 4 mm. A 135 filament with a diameter of 1.75 ± 0.1 mm was obtained by controlling the speed of 136 spool rotation and conveyer belts then the 3D printable filaments were collected by a 137 spool. 138



#### 140

# 141Figure 2. Composite filaments preparation via melt blending extrusion: the tables show the142parameters of screw profile and blending components proportions

143 2.2.3. 3D printing process

An open-source 3D printer named Mondrian 3.0 was used to print scaffold (20.1 × 144 20.1 × 3 mm) and standard dog bones (ISO 527, type 1A) using PLA/AT filaments at 145 146 190°C. Abundant of filament was needed to construct dog bone specimen, thus, we 147 prepared only one dog bone specimen due to the limited filament amounts. The 148 scaffolds were printed using PLA and PLA/AT composite filaments under three printing 149 temperature (180°C, 200°C, 220°C). The used printing parameters are shown in Table 1. 150 The scaffold and dog bone were designed by using a Slic3r program and printing process were controlled by Pronterface software. 151

152

Table 1. 3D printing parameters

Printing temperature	180 - 220°C
Layer height	0.2 mm
Infill density	100%
Infill pattern	linear
Layer angle	45°
Printing speed	12 mm/s

Nozzle diameter

#### 153 2.3. Characterizations

The acetylation of tannin was confirmed by NICOLET 6700 FT-IR spectrometer in attenuated total reflection (ATR) mode with a resolution of 4 cm<sup>-1</sup> and a total of 16 scans in the range 400-4000 cm<sup>-1</sup>.

Instron tensile testing machine (model 5569, Norwood, MA, USA) equipped with a 50 kN load cell was used for tensile strength tests with a cross-head speed 1 mm/min according to EN ISO 527:1996. The whole testing process was performed at room temperature and each sample has four repetitions. The tested dog-bone shaped specimens (ISO 527, type 1A) were previously molded with a micro-injection molder (Micro 15, DSM Xplore, Sittard, Netherlands).

A scanning electron microscopy (SEM, JSM-6490LV, Tokyo, JAPAN) with an acceleration voltage of 5 kV was applied to observe the morphology of a 3D printed scaffold. The scaffolds were sputter-coated with a thin layer of carbon before scanning.

A study on the thermal characteristics, in terms of the melting temperature (T<sub>m</sub>) and 166 crystallization temperature ( $T_c$ ), was undertaken under a nitrogen flow of 50 mL/min by 167 using a METTLER TOLEDO differential scanning calorimeter (DSC). A scanning rate of 168 10°C/min within the temperature range of 30°C to 220 °C and 220°C to -10°C in the 169 second scanning cycle was carried out. The measurements were conducted using 170 aluminum crucibles with a total sample weight of  $5.00 \pm 1$  mg. The values for melting 171 172 temperatures ( $T_m$ ), enthalpies of melting ( $\Delta H_m$ ) and crystallization ( $\Delta H_c$ ) were analyzed using STARe software.  $\Delta H_m^0$  is the enthalpy of melting for 100% crystallized PLA, which is 173 equal to 93.7 J/g (Yamoum et al., 2017), and w is the weight fraction of PLA. The 174 crystallization percentage ( $X_{c_2}$  %) was estimated using the following equation: 175

$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times w} \times 100\%$$
<sup>(1)</sup>

176 The degradation behavior of AT-filled PLA was characterized with the help of a 177 thermogravimetric analyzer (TGA, METTLER TOLEDO, Columbus, Ohio, USA) under air flow of 50 mL/min from 30 to 600°C. The heating rate was controlled at 10°C/min and
the weight of each sample was 5-10 mg.

**Color measurements.** PLA is a colorless and transparent polymer, thus, it generally 180 colorize with dyes (Hussain et al., 2015; Scheyer and Chiweshe, 2001). Tannin can 181 colorize PLA filaments due to its brown nature, which is a good feature for 3D printed 182 parts. The coloration of PLA filaments with acetylated tannin was investigated by a 183 spectrophotometer (X-rite, model 5P60, Regensdorf, Switzerland) based on the 184 185 international commission on illumination (CIE) system. Three parameters L\*, a\* and b\* were used to evaluate the colors of filaments, respectively. L\* represents the scale of 186 lightness, the value of 0-100 refers to perfect black to white. The value of a\* and b\* 187 stands for the color of the red-green and the yellow-blue character, respectively, in 188 189 which positive values represent redness or yellowness while negative values indicate greenness and blueness (Lai So et al., 2014). 190

191 Water absorption. The hydrophobicity of the filaments was characterized by 192 measuring their level of water absorption (Filgueira et al., 2017). Each filament was cut into a length of 70 ± 1 mm and submerged into 50 mL of distilled water in a plastic tube 193 194 for 30 days at room temperature. Before submerging the tested filaments into the water, the filaments were vacuum-dried for 6 h at 80°C and then measured the dried 195 weight (W<sub>0</sub>). After 30 days, the specimens were taken out from water and wiped using 196 filter paper. Then the weight was recorded as W<sub>1</sub>. The water uptake of PLA filaments 197 198 and AT-filled filaments was calculated according to the following equation:

Water absorption (%) = 
$$\frac{|W_1 - W_0|}{W_0} \times 100$$
 (2)

199Immersion in solvent. In order to understand the degradation of PLA/AT composites200in aquatic system, printed specimens of dimensions  $2.5 \times 30 \times 2$  mm were immersed in201buffer solutions (pH=4, pH=10) and PBS solution (pH 7.4) at 40°C for 50 days in an oven.202The initial weight (W<sub>0</sub>) of each specimen was recorded before soaking into the solvent in203glass tube containing 50 mL buffer solution. After 50 days, the samples were removed204from the tubes and washed 3 times with distilled water prior to final dry in oven at 40 °C

for 12 h. The weight of each specimen was denoted as  $W_1$ . The weight loss was calculated based on the equation (2).

#### 207 3. Results and discussion

#### 208 **3.1.** Characterization of acetylated tannin

209 The hydrophilic characteristic of tannin render it incompatible with hydrophobic or semi-hydrophobic polymers. This necessitates the modification of tannin for solving this 210 211 problem. Tannin acetylation was suggested to develop reasonable miscibility with PLA (Grigsby and Kadla, 2014). Figure 3 presents the FTIR spectra of tannin and tannin after 212 being acetylated. The spectrum of tannin reveals a broad band centered at 3250 cm<sup>-1</sup> 213 and can be ascribed to -OH stretching vibrations while the peak at 1614 cm<sup>-1</sup> refers to 214 215 aromatic ring stretching vibration. This latter signal corresponding to a function unaffected by the acetylation reaction which can be considered as an invariant band. 216 Compared to the band at 1614 cm<sup>-1</sup>, the sharp decrease of the -OH and emergence of a 217 new strong one at 1750 cm<sup>-1</sup>, which is typical of C=O stretching, representing ester 218 functional group, proves that the acetylation process was undertaken effectively (Luo et 219 al., 2010). Besides, the increased absorption at 1178 cm<sup>-1</sup> and 1044 cm<sup>-1</sup>, ascribed to C-O 220 stretching, is also in accordance with the structure of acetylated tannin (Smith, 2018; 221 222 Vila et al., 2016).



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224

Figure 3. FTIR spectra of tannin and acetylated tannin

#### 225 3.2. Mechanical properties of PLA/AT composites

226 The mechanical properties of PLA and PLA/AT composites are given in Figure 4. 227 Tensile strength of composite materials generally relies on the stress transfer capacity 228 between fillers and polymer matrix, which is significantly affected by the interfacial 229 adhesion of particle and matrix, particle size, as well as particle distribution (Fu et al., 230 2008). The dispersion of AT into a thermoplastic polymer without severe agglomeration 231 has been previously achieved by enhancement of the hydrophobic character of tannin 232 (Gaugler et al., 2007; Grigsby et al., 2013). Therefore, unlike native tannin-filled PLA (Anwer et al., 2015), PLA incorporated with 10% and 20% AT did not exhibit significant 233 effects on tensile strength of the resulting composites (Figure 4, a). While PLA 234 235 incorporated with 30% AT encountered a decrease of tensile strength because higher biopolymer content generally caused filler agglomeration during melt blending process 236 could result in poor particle distribution. Besides, higher loading of AT increases its 237 238 interfacial area with PLA, which worsens the situation especially in absence of interfacial adhesion due to lack of virtual chemical bonds between AT and PLA. A lower elongation 239 at break was noticed for PLA/AT composites compared with the neat PLA (Figure 4, b), 240 241 which again highlights the fact that the acetyl part as a modifying agent for tannin does 242 not possess any plasticizing effect to balance the developed interfacial adhesion as a 243 result of acetylation, which causes premature failure. In Figure 4 (c), Young's moduli increased as a function of AT loading since the filling component restricts the molecular 244 mobility of the polymeric chain yielding a better static adhesion (Wacker et al., 1998). A 245 246 similar result was previously noted for lignin-filled PLA system (Spiridon et al., 2015; Vila et al., 2016). 247



248

Figure 4. Tensile parameters of PLA/AT composites: tensile strength (a), elongation (b) and Young's modulus (c)

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#### 250 **3.3.** Differential scanning calorimeter

251 DSC was performed in order to detect the glass transition, crystallization and melting 252 temperatures of PLA and PLA/AT composites. DSC thermograms of PLA and PLA incorporated with various contents of AT are shown in Figure 5 and the results from the 253 254 second heating and first cooling cycles are collected in Table 2. The incorporation of AT 255 showed no significant effect on the melting  $(T_m)$  and the glass transition  $(T_g)$ 256 temperatures, are consistent with prior studies (Anwer et al., 2015; Grigsby et al., 2014; 257 Grigsby and Kadla, 2014). This means AT has little influence on intermolecular interactions or chain flexibility of PLA polymer chains (Müller et al., 2014). While the 258 259 enhancement of  $T_c$  refers to the composite filaments are more difficult to undergo cold 260 crystallization in comparison with pure PLA filaments and so require higher 261 temperatures (Dong et al., 2017). As can be found in Table 2, the crystallinity of PLA/AT 262 composites` is gradually decreasing with a corresponding decrease in the enthalpy of 263 crystallization as a function of AT content. Therefore, the PLA/AT composites became too amorphous to be more liable to undergo higher degradation rates. This feature 264 265 most likely benefits to the short-term application like implantable devices in biomedical 266 applications (Lyu and Untereker, 2009) since the degradation of PLA occurs during a generally long period (Karamanlioglu et al., 2017; Tokiwa and Calabia, 2006). 267



268

269

Figure 5.DSC thermograms of PLA and PLA/AT composites

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270

Table 2.	DSC results of	of PLA	and PLA/AT	composites
	<b>DJC</b> <i>i</i> C <i>JUi</i> C <i>j</i> C <i>i</i> C <i>j</i>	·) · • · · ·		composites

Sample	T <sub>g</sub> (°C)	$\Delta H_c$ (J/g)	T <sub>c</sub> (°C)	$\Delta H_m$ (J/g)	T <sub>m</sub> (°C)	X <sub>c</sub> (%)
PLA	56.7	14.2	120.2	20.4	152.5	6.6
9PLAT	56.3	4.23	127.5	10.9	152.6	7.9
8PLAT	56.8	0.78	129.4	3.01	151.9	3.0
7PLAT	58.6	0.26	129.7	0.06	151.1	

272

Note: "--" means that no crystallization percentage.

#### 273 3.4. Thermogravimetric analysis

The thermal behavior of PLA and PLA/AT composites was studied via 274 thermogravimetric analysis under air atmosphere. The weight loss and DTG data are 275 276 plotted in Figure 6as a function of temperature. Each sample sharply degraded in a one-277 step process started at 250°C and continued to 370°C, which is also corroborated from 278 the single peak in the DTG profile. The results demonstrated additionally that the incorporation of AT into to PLA matrix resulted in a decrease of the thermal stability, 279 280 presumably due to the drop in crystallinity (see Table 2). This observation is generally 281 found in PLA biocomposites (Boruvka et al., 2019; Grigsby et al., 2014; Zhang et al., 282 2017). The onset of degradation for all PLA/AT composites was very close to pristine 283 PLA (250°C) while the major decomposition took place at 350°C. Consequently, a 284 printing temperature below 250°C is considered suitable for PLA/AT composites and no 285 decomposition should be undertaken under these conditions.



Figure 6. Thermal gravimetric traces of PLA and PLA/AT composites (*a*) and their relevant DTG
 curves (*b*).

#### 288 **3.5.** Water absorption and degradation in solvent

PLA is a well-known degradable polymer, however, the total degradation of PLA into carbon dioxide, water, and methane in the environment generally lasts from several months to two years (Karamanlioglu et al., 2017). Moisture easily results in the hydrolyzation of PLA, therefore, water absorption capacity has been considered as an important factor to the degradability of PLA (Yew et al., 2005) when exposed to humid atmosphere. Degradation behavior of material in different pH condition is an important characteristic for many applications.

296 As presented in Figure 7 (a), PLA/AT composites exhibited a higher water absorption 297 compared with the neat PLA, which may result from the decrease of crystallinity. The 298 water absorption is related to its rate of diffusion into the composites and responsible for faster degradation of PLA/AT composites in various aqueous solutions (Figure 7, b). 299 This characteristic is positive for medical applications because the PLA-based implants 300 301 are firstly hydrolyzed in vivo by body fluids after absorbing water, which causes the 302 breaking of the ester bonds (Yew et al., 2005). In this study, the phosphate-buffered saline (PBS) solution (pH=7.4) was used to represent the body fluids in neutral 303

conditions, while phosphate buffer (pH=4.0) and sodium carbonate buffer (pH=10) are applied to investigate the degradation of composite material in acidic and basic conditions. All tested samples in aqueous environments exhibited higher degradation rate with increasing the AT content. The faster degradation that appeared in strongly basic condition is the easier random ester cleavage, whereas, under acidic conditions, it proceeds via chain-end cleavage, which is more time-consuming (Elsawy et al., 2017).



Figure 7. Water absorption of PLA with various AT contents over 30 days(a) and degradation in different solvent media over 50 days (b).

#### 310 **3.6.** PLA/AT composites for 3D printing application

Color is an important appearance factor for 3D printing products. As can be seen 311 from Table 3, PLA is a colorless transmitting polymer. The combination of PLA with dyes 312 313 for producing vibrant colors is necessary for commercial applications (Scheyer and 314 Chiweshe, 2001). From the optical image of the filaments (Table 3), PLA/ATcomposites displayed brown colors and lost transmitting characteristic. These composites had lower 315 L\* value which translates into a decrease of lightness. When PLA was compounded with 316 more AT, an increasing trend was observed from the increasing a\*and b\* values, 317 exhibiting more green hue and blue hue, respectively. Therefore, PLA/AT composites 318 could be promising colored filaments for 3D printing products. 319

320

Table 3. Color measurements of PLA and PLA/AT composite

sample Image of PLA and PLA/AT composites	L*	a*	b*
---	----	----	----

PLA	70.93	+0.91	+5.43
9PLAT	28.07	+7.91	+7.80
8PLAT	29.77	+9.09	+10.05
7PLAT	31.42	+10.22	+8.41

The model of dog bone specimens for tensile testing was used to evaluate the printability of PLA/AT composites, the printed specimens and their tensile strength results are collected in Table 4. The digital images of printed PLA/AT composites 324 revealed that the specimens exhibited some defects during printing, either underextrusions or in fill and outline separations. These printed issues are not only due to the 325 326 setting of the printing parameter but also may be caused by the imperfect dispersion 327 and agglomeration of the filler (Filgueira et al., 2017). Imperfect printing is commonly found in composite materials given that the presence of fillers in polymeric matrixes 328 329 change their characteristics and consequently affect their printability (Nguyen et al., 330 2018). Therefore, a correlation between the features of printing process with the ATfilled composite filaments is a key factor to obtain qualified printed objects. This issue 331 332 will be considered more intensively in our future work.

333 The materials derived from the melt-extrusion 3D printing process commonly showed a lower tensile strength compared to comparable specimens obtained by 334 traditional manufacturing methods (Cruz Sanchez et al., 2017). The relatively higher 335 porosity of the dog bones caused during 3D printing may probably justify this finding 336 (Filgueira et al., 2017). Another possible reason could be related to the poor interlayer 337 adhesion of the printed specimens because the mechanical properties of printed part 338 339 depends on the interlayer adhesion (Bakrani Balani et al., 2019). As a whole, the strength of printed specimen was very close to that processed by traditional 340 manufacturing methods (Figure 4). 341

342

#### Table 4. Printed dog bone specimens and their tensile parameters



For a specific material, the temperature is one of the most important parameters to control the shear viscosity and flow rate for offering successive layer deposition. The dimensional stability of each printed layer depends on the rapid solidification capacity via improved heat dissipation (Nguyen et al., 2018). Thus, the temperature should be carefully selected for validating the balance between flowability and solidification. For this purpose, the effects of temperature on the printability of PLA/AT composites and morphology of printed specimens were investigated by printing a scaffold prototype.

350 SEM images of the printed scaffolds at different temperatures are displayed in Table 351 5. Filaments made from PLA/AT composites are printable at a temperature range from 180 to 220°C. However, the surface morphology was mostly affected especially at higher 352 temperatures. It is worth to notice that both lower and higher printing temperatures 353 354 result in unsatisfying faults on the surface, namely, high roughness and phase separation, respectively, when PLA incorporated with a higher AT content (e.g. 7PLAT). 355 This highlights a strong correlation between high AT loading in the filaments and the 356 357 sensitivity to encounter phase separation at high temperatures. Similar results were 358 found for a system based on hemicellulose-filled filaments (Xu et al., 2018). The unsuccessful printing of PLA scaffold at 180°C is referred to the failure of the first layer 359 that should be stuck to the building platform. This might due to the fast cooling of 360 361 extruded PLA before bonding to the building platform or to the poor flowability of PLA at 180°C. In other words, the addition of AT reduced the melting viscosity of PLA 362 363 polymer (rheology behavior data in supplementary material, Figure S1), thus improved 364 the printability even at low temperature.

Table 5. SEM images of printed scaffolds at different 3D printing temperatures





#### 366 **4.** Conclusions

This study investigated the properties and 3D printability of a composite made from 367 PLA and acetylated tannin. The acetylation of tannin contributed to its well dispersion 368 within PLA matrix, guaranteeing successful fabrication of PLA/AT composite filaments 369 370 via a twin-screw extruder. PLA incorporated with 20 wt% acetylated tannin did not 371 significantly encounter deterioration in tensile property of the final product. Meanwhile, the incorporation of various AT contents caused no significant effect on the melting and 372 glass transition temperatures of PLA because it has little influence on intermolecular 373 interactions or chain flexibility of PLA polymer chain. A decrease of crystallinity was 374 found in PLA/AT composites, resulting in higher rates of degradation in aquatic system 375 especially under alkaline conditions, which would definitely benefit in short-term 376 applications like implantable devices in biomedical field. A 3D printing temperature 377

below 250°C is suggested for safe processing of PLA/AT composites without encountering decomposition according to the data of thermogravimetric analysis. Although PLA systems loaded with acetylated tannin showed good printability in general, this is limited to temperatures reasonably below 220°C to avoid printing defects caused by phase separation and aggregation of acetylated tannin, especially at high loading content.

384

#### 385 Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

388

#### 389 Conflict of interest

390 The authors declared that they have no conflicts of interest.

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400

#### 401 **5. References**

Ambrogi, V., Cerruti, P., Carfagna, C., Malinconico, M., Marturano, V., Perrotti, M.,
Persico, P., 2011. Natural antioxidants for polypropylene stabilization. Polym.
Degrad. Stab. 96, 2152–2158.
https://doi.org/10.1016/j.polymdegradstab.2011.09.015

- 406 Anwer, M., Naguib, H.E., Celzard, A., Fierro, V., 2015. Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin 407 particulate green composites. Compos Part В Eng 82. 92-99. 408 409 https://doi.org/10.1016/j.compositesb.2015.08.028
- Bajpai, P.K., Singh, I., Madaan, J., 2014. Development and characterization of PLAbased green composites: A review. J. Thermoplast. Compos. Mater. 27, 52–81.
  https://doi.org/10.1177/0892705712439571
- Bakrani Balani, S., Chabert, F., Nassiet, V., Cantarel, A., 2019. Influence of printing
  parameters on the stability of deposited beads in fused filament fabrication of
  poly(lactic) acid. Addit. Manuf. 25, 112–121.
  https://doi.org/10.1016/j.addma.2018.10.012
- Basu, A., Nazarkovsky, M., Ghadi, R., Khan, W., Domb, A.J., 2017. Poly(lactic acid)- based nanocomposites. Polym. Adv. Technol. 28, 919–930. https://doi.org/10.1002/pat.3985
- Boruvka, M., Behalek, L., Lenfeld, P., Ngaowthong, C., Pechociakova, M., 2019.
  Structure-related properties of bionanocomposites based on poly(lactic acid),
  cellulose nanocrystals and organic impact modifier. Mater. Technol. 34, 143–156.
  https://doi.org/10.1080/10667857.2018.1540332
- Bridson, J., Kaur, J., Zhang, Z., Donaldson, L., Fernyhough, A., 2015. Polymeric
  flavonoids processed with co-polymers as UV and thermal stabilisers for
  polyethylene films. Polym Degrad Stabil 122, 18–24.
  https://doi.org/10.1016/j.polymdegradstab.2015.10.002
- 428 Cruz Sanchez, F.A., Boudaoud, H., Hoppe, S., Camargo, M., 2017. Polymer recycling in
  429 an open-source additive manufacturing context: Mechanical issues. Addit. Manuf.
  430 17, 87–105. https://doi.org/10.1016/j.addma.2017.05.013
- 431 Dong, J., Li, M., Zhou, L., Lee, S., Mei, C., Xu, X., Wu, Q., 2017. The influence of
  432 grafted cellulose nanofibers and postextrusion annealing treatment on selected
  433 properties of poly(lactic acid) filaments for 3D printing. J. Polym. Sci. Part B
  434 Polym. Phys. 55, 847–855. https://doi.org/10.1002/polb.24333
- Elsawy, M.A., Kim, K.-H., Park, J.-W., Deep, A., 2017. Hydrolytic degradation of
  polylactic acid (PLA) and its composites. Renew. Sustain. Energy Rev. 79, 1346–
  1352. https://doi.org/10.1016/j.rser.2017.05.143
- Filgueira, D., Holmen, S., Melbø, J.K., Moldes, D., Echtermeyer, A.T., Chinga-Carrasco,
  G., 2017. Enzymatic-Assisted Modification of Thermomechanical Pulp Fibers To
  Improve the Interfacial Adhesion with Poly(lactic acid) for 3D Printing. ACS
  Sustain. Chem. Eng. 5, 9338–9346.
  https://doi.org/10.1021/acssuschemeng.7b02351
- Fu, S.-Y., Feng, X.-Q., Lauke, B., Mai, Y.-W., 2008. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. Compos. Part B Eng. 39, 933–961. https://doi.org/10.1016/j.compositesb.2008.01.002
- García, D., Glasser, W., Pizzi, A., Paczkowski, S., Laborie, M.-P., 2015. Modification of
   condensed tannins: from polyphenol chemistry to materials engineering. New J
   Chem 40, 36–49. https://doi.org/10.1039/C5NJ02131F
- García, D.E., Glasser, W.G., Pizzi, A., Paczkowski, S., Laborie, M.-P., 2015.
   Hydroxypropyl tannin from Pinus pinaster bark as polyol source in urethane

452	chemistry. Eur. Polym. J. 67, 152–165.
453	https://doi.org/10.1016/j.eurpolymj.2015.03.039
454	Gaugler, M., Grigsby, W., Harper, D., Rials, T., 2007. Chemical imaging of the spatial
455	distribution and interactions of tannin dispersal in bioplastic systems. Adv. Mater.
456	Res. 29–30, 173–176. https://doi.org/10.4028/www.scientific.net/AMR.29-30.173
457	Ge, J., Shi, X., Cai, M., Wu, R., Wang, M., 2003. A novel biodegradable antimicrobial
458	PU foam from wattle tannin. J. Appl. Polym. Sci. 90, 2756-2763.
459	https://doi.org/10.1002/app.12928
460	Gkartzou, E., Koumoulos, E.P., Charitidis, C.A., 2017. Production and 3D printing
461	processing of bio-based thermoplastic filament. Manuf. Rev. 4, 1.
462	https://doi.org/10.1051/mfreview/2016020
463	Grigsby, W., Bridson, J., Lomas, C., Frey, H., 2014. Evaluating Modified Tannin Esters
464	as Functional Additives in Polypropylene and Biodegradable Aliphatic Polyester.
465	Macromol Mater Eng 299, 1251–1258. https://doi.org/10.1002/mame.201400051
466	Grigsby, W., Kadla, J., 2014. Evaluating Poly(lactic acid) Fiber Reinforcement with
467	Modified Tannins. Macromol Mater Eng 299, 368–378.
468	https://doi.org/10.1002/mame.201300174
469	Grigsby, W.J., Bridson, J.H., Lomas, C., Elliot, JA., 2013. Esterification of Condensed
470	Tannins and Their Impact on the Properties of Poly(Lactic Acid). Polymers 5,
471	344–360. https://doi.org/10.3390/polym5020344
472	Grigsby, W.J., Bridson, J.H., Schrade, C., 2015. Modifying biodegradable plastics with
473	additives based on condensed tannin esters. J Appl Polym Sci 132, 41626.
474	https://doi.org/10.1002/app.41626
475	Guo, R., Ren, Z., Bi, H., Song, Y., Xu, M., 2018. Effect of toughening agents on the
476	properties of poplar wood flour/poly (lactic acid) composites fabricated with
477	Fused Deposition Modeling. Eur. Polym. J. 107, 34-45.
478	https://doi.org/10.1016/j.eurpolymj.2018.07.035
479	Hussain, T., Tausif, M., Ashraf, M., 2015. A review of progress in the dyeing of eco-
480	friendly aliphatic polyester-based polylactic acid fabrics. J. Clean. Prod. 108,
481	476–483. https://doi.org/10.1016/j.jclepro.2015.05.126
482	Kai, D., Tan, M.J., Chee, P.L., Chua, Y.K., Yap, Y.L., Loh, X.J., 2016. Towards lignin-
483	based functional materials in a sustainable world. Green Chem. 18, 1175-1200.
484	https://doi.org/10.1039/C5GC02616D
485	Karamanlioglu, M., Preziosi, R., Robson, G.D., 2017. Abiotic and biotic environmental
486	degradation of the bioplastic polymer poly(lactic acid): A review. Polym. Degrad.
487	Stab. 137, 122–130. https://doi.org/10.1016/j.polymdegradstab.2017.01.009
488	Koleckar, V., Kubikova, K., Rehakova, Z., Kuca, K., Jun, D., Jahodar, L., Opletal, L.,
489	2008. Condensed and hydrolysable tannins as antioxidants influencing the health.
490	Mini Rev. Med. Chem. 8, 436–447. https://doi.org/10.2174/138955708784223486
491	Lai So, V.L., He, L., Xin, J.H., 2014. Bio-inspired colouration on various textile
492	materials using a novel catechol colorant. RSC Adv 4, 41081-41086.
493	https://doi.org/10.1039/C4RA06004K
494	Lee, JY., An, J., Chua, C.K., 2017. Fundamentals and applications of 3D printing for
495	novel materials. Appl. Mater. Today 7, 120–133.
496	https://doi.org/10.1016/j.apmt.2017.02.004
497	LI, T., Aspler, J., Kingsland, A., 2016. 3D PRINTING - A REVIEW OF

498	TECHNOLOGIES, MARKETS, AND OPPORTUNITIES FOR THE FOREST
499	INDUSTRY. Can. Makes. URL http://canadamakes.ca/3d-printing-review-
500	technologies-markets-opportunities-forest-industry/ (accessed 12.4.19).
501	Liao, J., Brosse, N., Pizzi, A., Hoppe, S., 2019. Dynamically Cross-Linked Tannin as a
502	Reinforcement of Polypropylene and UV Protection Properties. Polymers 11, 102.
503	https://doi.org/10.3390/polym11010102
504	Liu, J., Sun, L., Xu, W., Wang, Q., Yu, S., Sun, J., 2019. Current advances and future
505 506	perspectives of 3D printing natural-derived biopolymers. Carbohydr. Polym. 207, 297–316. https://doi.org/10.1016/j.carbpol.2018.11.077
507	Long, H., Wu, Z., Dong, O., Shen, Y., Zhou, W., Luo, Y., Zhang, C., Dong, X., 2019.
508	Mechanical and thermal properties of bamboo fiber reinforced
509	polypropylene/polylactic acid composites for 3D printing. Polym. Eng. Sci. 59.
510	E247–E260. https://doi.org/10.1002/pen.25043
511	Luo, C., Grigsby, W., Edmonds, N., Easteal, A., Al-Hakkak, J., 2010. Synthesis,
512	characterization, and thermal behaviors of tannin stearates prepared from
513	quebracho and pine bark extracts. J. Appl. Polym. Sci. 17, 352–360.
514	https://doi.org/10.1002/app.31545
515	Lyu, S., Untereker, D., 2009. Degradability of Polymers for Implantable Biomedical
516	Devices. Int. J. Mol. Sci. 10, 4033-4065. https://doi.org/10.3390/ijms10094033
517	Müller, A.J., Ávila, M., Saenz, G., Salazar, J., 2014. CHAPTER 3. Crystallization of
518	PLA-based Materials, in: Jiménez, A., Peltzer, M., Ruseckaite, R. (Eds.), Polymer
519	Chemistry Series. Royal Society of Chemistry, Cambridge, pp. 66-98.
520	https://doi.org/10.1039/9781782624806-00066
521	Murariu, M., Dubois, P., 2016. PLA composites: From production to properties. Adv.
522	Drug Deliv. Rev., PLA biodegradable polymers 107, 17–46.
523	https://doi.org/10.1016/j.addr.2016.04.003
524	Nguyen, N.A., Barnes, S.H., Bowland, C.C., Meek, K.M., Littrell, K.C., Keum, J.K.,
525	Naskar, A.K., 2018. A path for lignin valorization via additive manufacturing of
526	high-performance sustainable composites with enhanced 3D printability. Sci. Adv.
527	4, eaat4967. https://doi.org/10.1126/sciadv.aat4967
528	Nicollin, A., Zhou, X., Pizzi, A., Grigsby, W., Rode, K., Delmotte, L., 2013. MALDI-
529	TOF and 13C NMR analysis of a renewable resource additive—Thermoplastic
530	acetylated tannins. Ind. Crops Prod. 49, 851–857.
531	https://doi.org/10.1016/j.indcrop.2013.06.013
532	Olejar, K.J., Ray, S., Kilmartin, P.A., 2016. Enhanced antioxidant activity of polyolefin
533	films integrated with grape tannins: Enhanced antioxidant activity of polyolefin
534	films integrated with grape tannins. J. Sci. Food Agric. 96, 2825–2831.
535	$\frac{1000}{10.1002/jsta./450}$
536	Pizzi, A., 1980. Tannin-Based Adnesives. J. Macromol. Sci. Part C 18, $247-315$ .
537	1000000000000000000000000000000000000
538	Ren, J., 2011. Biodegradable poly (lactic acid) synthesis, modification, processing and
539	applications. I singnua University Press. Springer, Beijing, Heidelberg.
54U	Samper, W.D., Fages, E., Fenomar, U., Boronar, I., Balarr, K., 2015. The potential of
541	navonoids as natural antioxidants and U v right stabilizers for polybropyiene. J.
E /I ·	Appl Dolum Sci 120 1707 1716 $https://doi.org/10.1002/opp.20071$
54Z	Appl. Polym. Sci. 129, 1707–1716. https://doi.org/10.1002/app.38871 Schever, J. E., Chiweshe, A., 2001, Application and Performance of Disperse Dyes, or

544	Polylactic Acid (PLA) Fabric. AATCC Mag. 1, 44–48.
545	Shnawa, H., Khaleel, M., Muhamed, F., 2015. Oxidation of HDPE in the Presence of
546	PVC Grafted with Natural Polyphenols (Tannins) as Antioxidant. J. Polym. Chem.
547	05, 9–16. https://doi.org/10.4236/ojpchem.2015.52002
548	Smith, B.C., 2018. The C=O Bond, Part IV: Acid Anhydrides [WWW Document]. URL
549	http://www.spectroscopyonline.com/co-bond-part-iv-acid-anhydrides (accessed
550	4.16.19).
551	Tappa, K., Jammalamadaka, U., 2018. Novel Biomaterials Used in Medical 3D Printing
552	Techniques. J. Funct. Biomater. 9. https://doi.org/10.3390/jfb9010017
553	Tokiwa, Y., Calabia, B.P., 2006. Biodegradability and biodegradation of poly(lactide).
554	Appl. Microbiol. Biotechnol. 72, 244-251. https://doi.org/10.1007/s00253-006-
555	0488-1
556	Tomak, E.D., Arican, F., Gonultas, O., Sam, E.D., 2018. Influence of tannin containing
557	coatings on weathering resistance of wood: Water based transparent and opaque
558	coatings. https://doi.org/10.1016/j.polymdegradstab.2018.03.011
559	Vila, C., Santos, V., Saake, B., Parajó, J.C., 2016. Manufacture, Characterization, and
560	Properties of Poly-(lactic acid) and its Blends with Esterified Pine Lignin.
561	BioResources 11, 5322–5332. https://doi.org/10.15376/biores.11.2.5322-5332
562	Xu, W., Pranovich, A., Uppstu, P., Wang, X., Kronlund, D., Hemming, J., Öblom, H.,
563	Moritz, N., Preis, M., Sandler, N., Willför, S., Xu, C., 2018. Novel biorenewable
564	composite of wood polysaccharide and polylactic acid for three dimensional
565	printing. Carbohydr. Polym. 187, 51–58.
566	https://doi.org/10.1016/j.carbpol.2018.01.069
567	Yamoum, C., Maia, J., Magaraphan, R., 2017. Rheological and thermal behavior of PLA
568	modified by chemical crosslinking in the presence of ethoxylated bisphenol A
569	dimethacrylates 28, 102–112. https://doi.org/10.1002/pat.3864
570	Yew, G.H., Mohd Yusof, A.M., Mohd Ishak, Z.A., Ishiaku, U.S., 2005. Water absorption
571	and enzymatic degradation of poly(lactic acid)/rice starch composites. Polym.
572	Degrad. Stab. 90, 488–500.
573	https://doi.org/10.1016/j.polymdegradstab.2005.04.006
574	Zhai, Y., Wang, J., Wang, H., Song, T., Hu, W., Li, S., 2018. Preparation and
575	Characterization of Antioxidative and UV-Protective Larch Bark Tannin/PVA
576	Composite Membranes. Molecules 23, 2073.
577	https://doi.org/10.3390/molecules23082073
578	Zhang, L., Lv, S., Sun, C., Wan, L., Tan, H., Zhang, Y., 2017. Effect of MAH-g-PLA on
579	the Properties of Wood Fiber/Polylactic Acid Composites. Polymers 9, 591.
580	https://doi.org/10.3390/polym9110591
581	
582	